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Electro-Analysis of Copper-Nickel, Chromium-Copper and Chromium-Copper-Nickel Alloys

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ELECTRO-ANALYSIS
OF
COPPER-NICKEL, CHROMIUM-COPPER
AND
CHROMIUM-COPPER-NICKEL ALLOYS

BY

SIDNEY MARION HULL

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

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May 25, 1915

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Sidney Marion Hull

ENTITLED ELECTRO-ANALYSIS of COPPER-NICKEL, CHROMIUM-COPPER, and CHROMIUM-COPPER-NICKEL ALLOYS.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE, in Chemistry

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ELECTRO-ANALYSIS
of
COPPER-NICKEL, CHROMIUM-COPPER
and
CHROMIUM-COPPER-NICKEL
ALLOYS

INTRODUCTION

The quantitative estimation of metals by electrolysis is today of such importance in the chemical world as to leave no question of its availibility or practicableness. A wealth of data in regard to this phase of chemistry is to be found in most of the textbooks on the subject of quantitative analysis, and very complete accumulations of the data which has appeared from time to time in the various journals have been made into book form by men pursuing research along these lines. Nevertheless, as it is well known to any one who has tested out the various methods which are given in current literature in any field, many applications of a reaction or operation are made and published without the author's being convinced of their thorough practiability. This being true, it remains with the individual worker in each field to test out these methods and select from those which appear to be the most highly recommended for the work, the ones which seem to give the most consistent results and reliability of data.

Therefore, although much work has been done along the same lines as the following investigation, it seems to the author that there is still room for selection to be made, and many points in the technique of operation to be worked out, which, together with new improvements which suggest themselves from time to time, would

tend to make the electro-analysis of metals somewhat easier for the man who has had no experience in this field, which at best, is a rather difficult one for the inexperienced operator.

PRESENT STATUS OF THE FIELD.

Concerning the deposition of copper, nickel and chromium, more work has been done on the first two, than upon any other metals commonly determined in this manner, and it is only with chromium that there appears to be any doubt in regard to the feasibility of this method of analysis. Copper is far more easily deposited from an acid electrolyte than from any other solution, a sulfuric acid solution being the one usually recommended for this type of work. Nitric acid may also be used, when copper alone is present. Edgar F. Smith, in his book on electro-analysis, gives several other methods which he has gathered from various sources, chief of which are those using ammoniacal or ammonium oxalate solutions. The first is open to the objection that the deposit is apt to be spongy and not easily washed and weighed. It is also somewhat slower than with the acid bath. On the other hand, he claims that by its use, he can deposit the copper quantitatively in the presence of chlorides, which is not possible in an acid solution. The use of ammonium oxalate is never to be recommended, as it will invariably break down and give a deposit of free carbon along with the copper, thus materially increasing the weight of the deposit. It also makes a turbid solution, which from the standpoint of the analyst is unsightly and gives a bad impression as to the reliability of the work.

In the case of the determination of the nickel, however,

there seems to be only one electrolyte which has stood the test of time and conditions which has been imposed upon it, viz., the ammoniacal-ammonium sulfate solution. W. Judson Marsh[*] gives the results of a number of experiments conducted by him on the various methods which have been suggested from time to time for the electrolytic determination of this metal, and sums up by saying that of all the methods tried, the only one which gave complete satisfaction in all cases, was the one using this electrolyte. All those, in which organic acids were used, were decomposed with the liberation of free carbon, as in the case of copper. Those in which an acid electrolyte was used, having a low concentration of the H ion, (for it is only under this condition that Nickel can be plated out from an acid solution) were so slow as to be prohibited from that standpoint alone. Others exhibited the phenomenon of "burning" at the end, when the concentration of the Ni ion became low. These complicated electrolytes may be quite suitable for the electrolysis of a salt dissolved in water, where the conditions can be fixed for the reaction. However, in the case of an alloy dissolved in an excess of concentrated acid, there is so much acid to be neutralized and so much salt formed by this neutralization, that it is almost impossible to get the exact conditions prescribed. This constitutes the greatest objection to their use.

There is less data in regard to the electrolytic determination of chromium than of either of the other two metals treated in this paper, and hence it offers more room for original investigation. According to Meyers, it can be determined with the use of a mercury cathode where the acidity is not excessive,using a

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[*] Trans. Amer. Electro-Chem. Soc., 26, 79(1914)

platinum anode and a current of from one to three amperes.*

*Jour. Amer. Chem. Soc., 26, (1128)

Under these conditions, the chromium separates out as an amalgam with the Hg., and can be determined by the increase in weight of the latter. Various other metals have been determined by this means, and the method seems at first to be entirely practical, but it has the one great drawback that, the chromium amalgam is very unstable and will decompose almost immediately in the presence of water. The chromium separates out on the suffface of the mercury as a fine black powder, Cr_2O_3, which of course, introduces the error of the amount of oxygen necessary to combine with the chromium. There are more objections to this proceedure, which will be taken up under the discussion of the experimental work on this metal.

Finally, there is the almost total absence of methods for the determination of a seried of metals in the same sample of solution. The problem presented by the presence of these three metals in the same sample, and the electrolysis of each in the presence of the others, or after the others have been removed, is very different from dissolving up a weighed amount of a pure salt in water, and electrolyzing it with close control of acid concentration and other conditions. It is the aim of the author in the present instance to develope a means of quantitatively removing one metal after another from the same sample, using the residues of one determination as the material for the next. This of course, prohibits the removal or loss of any of the solution up to the time of the last deposition.

III. APPARATUS

The apparatus first used was the type ordinarily found in modern laboratories fitted for this variety of work, and consisted of a ringstand fitted with a revolving anode connected to a power driven shaft. The anode itself was a simple platinum spiral, with a stem, centered, to make the revolution as true as possible. Even with the heavy grade of wire used, great care was necessary to keep the spiral from getting out of center, when the lower end would whirl out in a circle and come in contact with the cathode. This was obviated by the sealing of a glass wire on the stem, leaving only enough space on the wire at the top to use as an insert into the revolving connection, and extending down to the spiral at the lower end. The cathode used with this type of apparatus was the ordinary platinum cylinder, about three cms. in diameter and six to eight cms. long. This gave fairly satisfactory results when the conditions for the electrolysis were exact, and there was no tendency to spongy deposits, but even with an anode speed of as high as 600 revolutions per minute, the liquid could not be agitated fast enough to avoid a spongy deposition when the acid concentration was slightly high, or some other condition was not quite as prescribed. This apparatus did not seem to be suited to the needs of the person doing ordinary commercial work on alloys, who can not take the time or trouble to bring his sample to the exact requirements demanded in this case.

Consequently, after some little work with this set-up, another method was sought which would more nearly fulfill the demands of the rapid worker. This was found in the combination of two

suggestions from different sources:, first, the use of a gauze cathode with the same type of anode, and second, the solenoid as the means of rotation of the liquid.

Platinum gauze cathodes have been used for some time in determinations of this type, but on account of their cost and the ease with which the inexperienced worker may injure them, their use has not been very extensive in this country. But in the article cited above by Marsh, in his paper on the electrolysis of Nickel,the use of copper gauze with a Platinum wire as a stem to connect with the binding post was recommended. From this suggestion, gauze cathodes were made of copper screening 40 meshes to the inch, cut in strips 4½ cms. wide by 12 cms. long, which were bent into cylinders and fastened with a copper wire of about 14 gauge,passed through the overlapping edges of the joint. This was cut long enough to project over the edges of the gauze for a distance of 7 cms., making a stem to connect with the binding post. Such an arrangement makes a very satisfactory cathode on which to deposit copper and Nickel, as well as various other metals, which although they do not come within the scope of this paper, still make an interesting and valuable addition to the list. The author has used such a type for the determination of tin, zinc, and cobalt, and found them to give excellent results in all cases, while Marsh himself, claims that they may also be used for the determination of cadmium and bismuth, as well as in connection with the Platinum wire gauze anodes for lead and manganese. In this case, of course, the copper could not be used as an anode on account of its solution tension in such a position. The only place in which they did not come up to all the requirements demanded of them,

was in an ammoniacal solution, where the ammonia fumes would attack the copper stem and cause a soluble compound to form, which, not washing off in time to be plated out again, caused a loss in weight to take place, thus giving a low result to the determination. Hence, in order to use this type of electrode for the electrolysis of Nickel, or other metals in an ammoniacal solution, it was necessary to protect it from attack by coating the stem with some material which would be acid- and alkali- proof and of constant weight throughout the experiment. Several materials were tried, such as asphalt and shellac, but the best results were obtained by a coat of Bakelite varnish. After heating this at 140°C and then applying a second coat and baking at the same temperature for 3-4 hours, it made an acid-and ammonia-proof coat which would retain a constant weight throughout the life of the gauze and effectually protect it from corrosion. The only place in which such a coating could not be used was in the determination of zinc from a solution of sodium zincate, where the strong alkali, while not dissolving the Bakelite, would loosen the coat and cause it to peel off, thus ruining the determination. But in such a case, the bare copper wire can be used without fear of its being attacked, so that with two sets of cathodes, those with the Bakelite and those with the copper stem alone, a non-platinum electrode is available which will suffice for all ordinary determinations. When the surface of the wire gauze becomes so coated with the metal that no furthur deposit is feasible, it can be very easily cleaned by dipping for a few moments into 1-1 HNO_3, and then washing thoroughly, whidh on rinsing in alcohol and drying at 100°C, leaves a smooth, bright surface on which to deposit more metal. Such an electrode, if care is used

in cleaning, will last from 25-30 determinations, and provides, for a few cents each, a substitute for the expensive platinum gauze cathode.

Such a cathode should be made to suit the requirements of the beaker in which the electrolysis is th be carried out, as the amount of stirring in the cell, due to the action of the solenoids, is proportional to the length of radius in which the lines of force have a chance to exert a torque on the liquid through which the current is passing. Hence, the cathode should be made to fit closely the inside of the beaker, which should be small enough to cover the entire cathode with that volume at which the electrolysis is to be made. The stem should also be long enough to allow the base of the cathode to come close to the bottom of the beaker, as the magnetic field is stronger, the more nearly the end of the magnet is approached, and thus, as before, a greater force is exerted to produce rotation.

The solenoids, which were used in the following experiments, were made of 200 feet of No. 18 Cu. wire,cloth insulated, wound with approximately 1000 turns around an iron core, 2cms. in diameter by 20 cms. long, Through this was passed a direct current of five amperes, which produced at the end of the iron core, a field intensive enough to cause a rotation, equal to, if not greater than that produced by the platinum spiral, rotating at a speed of 600 revolutions per minute. An early description[*] of this device directs that the wire be wound on a copper cylinder, large enough to permit the placing of the beaker within the coil, thus allowing the lines of force to pass directly through the liquid,

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[*] Jour. Amer. Chem. Soc., 29, 1592, (1907) Frary.

which produces such a violent stirring effect as in some cases to throw the liquid out of the beaker. But this was objectionable from the fact that the operator could not view the electrolysis and also that it would heat the solution to the boiling point, thereby causing frothing and loss of liquid. A modification of this scheme[*] was proposed in 1912 by Knot and Work, who claimed that by placing the cell at the top of the solenoid, enough rotation could be obtained to give all the advantages of the process with none of the disadvantages. The writer has found this to be the case, with the added fact that although this type of rotator does heat up the electrolyte to a certain extent, the heating is not excessive, but on reaching a temperature of 70-80 degrees, the radiation loss prevents furthur rise. The electrolysis is thus conducted at a temperature which is most suitable for the maximum efficiency of the current used, together with the production of a smoother deposit than could be obtained at a lower temperature.

From the accompanying photograph and diagram, it may be seen that the apparatus and wiring is of an extremely simple nature, ring stands being used for the supports of the electrodes, which were insulated from the stands by passing them through rubber stoppers. The current was obtained from ten, two volt storage cells placed in series, providing a twenty volt circuit which could be cut down to the required amount by the resistances. A system of wiring was also devised, such that by placing the two cell circuits in parallel, the voltage and amperage of each could be measured without interference with the action of the other. The solenoids were entirely independent of this circuit, since when using a low

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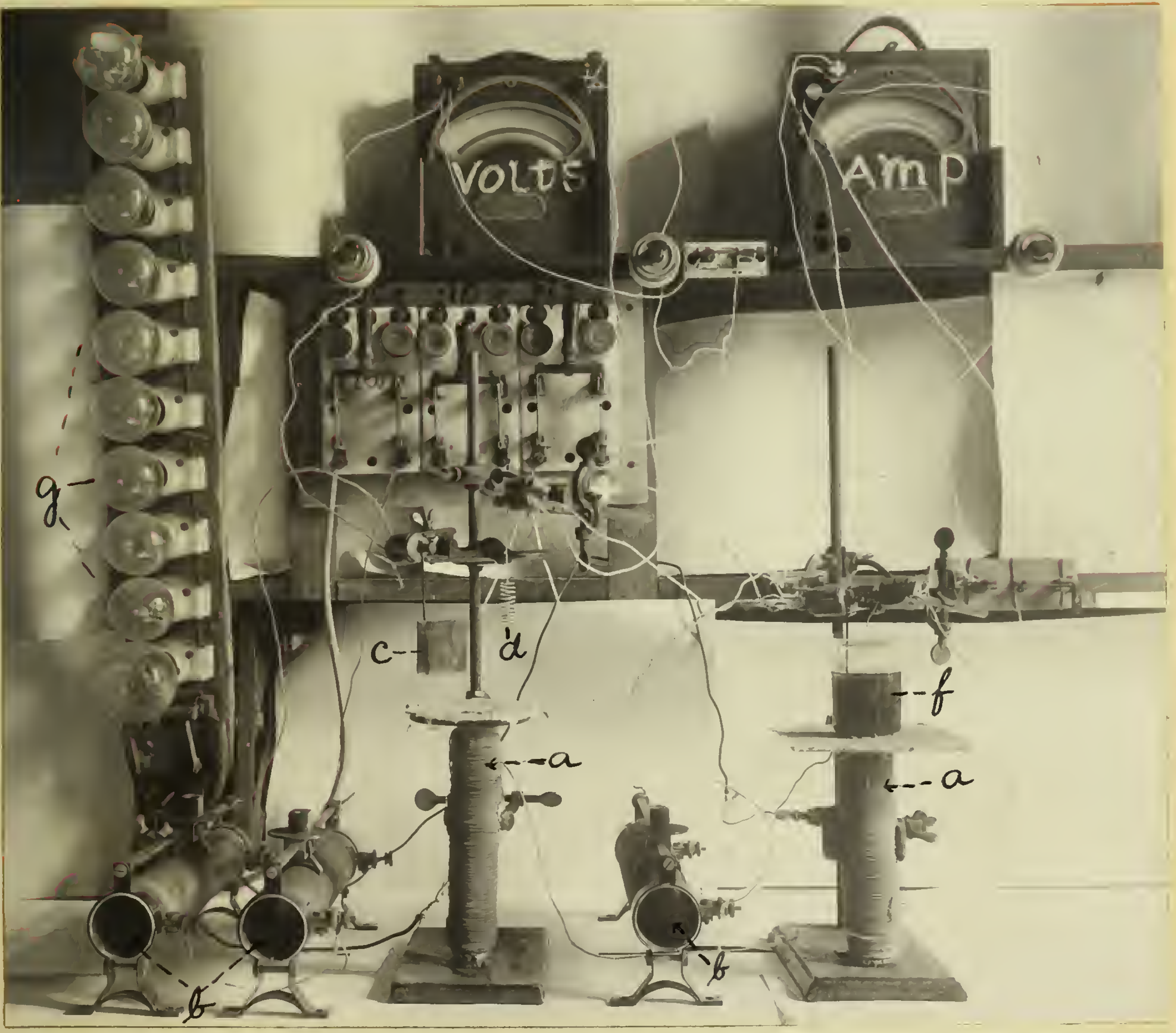
[*] Jour. Ind. and Eng. Chem., 4, 534, (1912)

Photograph of the Electrolysis Apparatus as described on page 9.



a,a, --- Solenoids.

b,b,---- Resistances.

c,------ Gauze cathode.

d,------ Platinum spiral anode.

f,------ Cell in operation.

g,-----lamp bank to reduce the 110 volt circuit for the solenoids.

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current through the cell, it was thus possible to obtain a maximum stirring effect, which, although small, was much greater than if the solenoids and electrolysis apparatus had been placed in series and the same current passed through both.

IV. PREPARATION OF THE ALLOY FOR ELECTROLYSIS.

In sampling the alloy, three different methods were tried: (a) sawing off a solid piece from the end; (b) drilling out the end and saving the drillings; and (c), turning the castings on a lathe and saving the turnings after the outer oxidized crust had been removed. The first method was applicable for the alloys containing only copper and nickel, as they were sufficiently soluble in acids to make this a practicable form in which to dissolve them. The second was a rather difficult operation, as the alloys were cast in long slender bars, about one cm. in diameter, and after getting higher in the chromium content, the alloys became so hard, that without the use of oil, which was very objectionable in the sample, it was almost impossible to drill them out and keep the drill centered in the piece. Still furthur up in the series the drill would not touch them at all. Hence the only method which could be used was turning them in the lathe, which seemed to give very satisfactory results, both in the homogeneity of the metal and the form for solution. Several samples were taken from the same casting in the various ways mentioned, and in all cases were found to check up with each other exactly, which however, would not have been the case if the alloy had not been homogeneous throughout. This is quite as important from the standpoint of the prop-

erties of the casting as from that of the analyst, for it is a sure way of testing the constitution of the metal, as to whether there has been any segregation.

The weight of the sample taken was in the majority of cases, about ten grams, which precluded any danger of getting a sample not representative of the entire piece. Those containing copper and nickel alone were then placed in 500cc. Erlenmeyer flasks and heated on a water bath with HNO_3 till complete solution and evaporation to dryness had taken place. For those which contained chromium, this method would not suffice because of the formation of an oxide film on the metal. If HNO_3 were kept out until all the chromium had been dissolved with HCl, it could then be added and the whole treated the same as the other samples. The evaporation was hastened by the blowing of a current of air in at the top of the Erlenmeyer flasks from a glass tube made for the purpose by blowing holes in the sides at right spaces along the tube, and laying the whole along the top of the flasks placed in a row on the waterbath. Sufficient H_2SO_4 was then added to decompose all the chlorides and nitrates, together with 15-20 ccs. excess, and this was again heated on the bath to drive off as much of the volatile acid fumes as possible. The flask was then placed in an ordinary ringstand clamp and agitated over a low flame, when the remainder of the fumes was driven off, and the solution, or rather, the almost solid mass of salt, was evaporated down to SO_3 fumes to remove the last traces of the other acids. This is a rather difficult thing to do and one that requires considerable patience on the part of the operator, as the flask must be heated up slowly and constantly agitated with quick, sharp jerks to keep the

pasty mass in the flask from bumping and consequent loss. The evaporation of the material to SO_3 fumes was very essential in this series, as chlorides were prohibited in the electrolysis of copper, and nitrates in that of nickel. Hence, the sulfate was the only form in which the metals could be obtained without the necessity of removing a radical during a run for the three metals.

As soon as the flask was sufficiently cool, water was added, and the whole boiled to get the salt into solution, a rather difficult thing to do when chromium was present in the mass, since, during the evaporation, the $Cr_2(SO_4)_3$ was almost completely dehydrated, and long continued boiling was necessary to get the hydrated form, which alone is appreciably soluble. This solution was then made up to volume, and an aliquot of 100 cc. taken for analysis.

V. RESULTS OF THE INVESTIGATION ON THE METHODS OF PROCEDURE FOR THE INDIVIDUAL METALS, AND THE DIFFICULTIES INVOLVED.

(a) Copper. As suggested above, the most applicable method for the determination of copper, was that using a straight acid solution with the acid concentration varying from 1-5 cc. per hundred ccs. of volume. This last would probably have been excessive with the use of the ordinary form of cathode, but with the gauze form and the proper agitation, even at the high current of three amperes which was used in all cases, the deposit was firm and coherent. One to two grams of urea were also added to form addition products with the metal, and thus help to make the deposit more

smooth. On experiments to determine the rate of deposition at three amperes and approximately four volts, it was found that one hour was sufficient to complete the deposition of one gram of copper, To remove the last traces from the solution took a much longer time in proportion to the amount of metal deposited than did the deposition at the beginning of the operation. From this, knowing roughly the amount of copper in the solution,the time was calculated for each case, and the current allowed to run for five minutes in excess of this time, in order to be sure that in each case all the copper had been electrolyzed. Since the color of the Copper sulfate was so nearly that of the Nickel and Chromium solution, no means was obtainable of telling when the endpoint was reached, by the color of the liquid. Its removal from the beaker for testing outside the cell was prohibited by the fact that the same sample of liquid was to be used for both the determination of the nickel and chromium. This was also a bad point in the electrolysis of the nickel, and the time factor was the only criterion of endpoint used throughout the entire set of experiments.

Great care must be taken here to remove the copper completely from the solution, for if this is not done, it will be deposited along with the nickel, in the ammonium electrolyte, and although this would cause error in the determination of the copper and nickel both, it would not be detected from the fact that the total of the constituents would add up to 100% as before.

(b) Nickel. The ammoniacal solution of nickel sulfate was the one favored in the following as being the most highly recommended both on account of its rapidity and the ease with the electrolyte may be prepared from the residues left in the determination

of the copper. In the electrolysis of the copper-nickel series, the washings and residues from the copper were evaporated down to a small volume, the acid neutralized with ammonia, and twenty five cc. excess added. Also 3-4 grams of $(NH_4)_2SO_4$. This was then electrolyzed at three amperes and four volts the same as the copper.

This was the most satisfactory deposition made through out the series, the metal coming down rapidly and smoothly, so firm in fact, that ten to twelve deposits could be made on one electrode without necessitating the removal of any of the adhering metal. This saved considerable time, since the final weight of one would be the initial weight of the next. As mentioned above, it was necessary to use the cathode with the Bakelite coated stem in all these determinations, while the scheme of telling the end point of the reaction by allowing the current to flow for a short time in excess of the amount required by the rough estimation of the metal, was used in all cases. This electrolysis was not as rapid as that of the copper, one and one half hours being necessary for the deposition of one gram. But it was by far the most easily controlled and operated of any encountered. When the nickel was alone present, the end point could be told with great accuracy by the addition of a drop of dimethyl glyoxime to some of the solution, outside of the cell.

In the presence of chromium sulfate, this procedure had to be varied somewhat, as the chromium interefered with the complete deposition of the nickel. It was naturally expected that the addition of ammonia to the solution of the chromium salt would precipitate the chromium as $Cr(OH)_3$, Such was not the case where the solution had been evaporated to SO_3 fumes and had not been allowed

to stand for several days. For the dehydrated chromium sulfate seemed to form a complex ion in the presence of ammonia, and would not be precipitated without long continued boiling or standing, when it would come down in the usual form.

However, with this difficulty out of the way, the chromium seemed to prevent the deposition of the nickel, either changing from the chromous to the chromic state and back again, as iron does, or else oxidizing to a chromate and thus preventing the deposition by its action. This last was proved to be the case in an acid solution, for when the electrolyte was made slightly acid with acetic acid, in which condition the nickel will plate out slowly if alone, the chromium was oxidized to the chromate condition, as was clearly shown by the yellow color of the solution. This was proved to be the retarding agent by the fact that when all the chromate was precipitated by $BaCl_2$ placed in the solution, the nickel was completely deposited. This method was not a feasible one for its determination, however, since enough $BaCl_2$ had to be added to precipitate all the sulfate in the solution before any was available to react with the chromate, and with such a large amount of precipitate present, the nickel could not be quantitatively determined.

Since the above was true, various reducing agents were introduced into the solution to keep the chromium in the chromic state. Of these it is only necessary to mention one of each type, to show all the various agents used to accomplish this result. Since any aliphatic aldehyde that could be easily obtained would not remain in solution at the temperature at which the electrolysis was conducted, an aromatic one, benzaldehyde, was used on sev-

eral samples to keep the chromium reduced. This seemed to accomplish the desired result fairly well, but on account of its non-volatility and high molecular weight, it was decomposed during the process with the production of free carbon. This so over-clouded the cell and all its contents that the deposit could not be washed free from the foreign matter present and as, in such cases, carbon is always deposited along with the metal on the cathode, it is probable that the result would not have been reliable. Alcohols, hydroquinone, glucose and hydrazine sulfate were all tried with varying results. Some would not accomplish the reduction at all, others would reduce the chromium somewhat, but would liberate free carbon as did the benzahldehyde, while most of them would froth and run out of the beaker. Hence, after trying these most active reducing agents that could be obtained and getting no results, it was decided that such a separation could not be made without the results of a research which would involve more time and apparatus than could be spent on the problem in the limited time available. Hence, when those alloys which contained both nickel and chromium were analyzed, the chromium was first removed by precipitation as $Cr(OH)_3$, and the nickel determined in the filtrate and washings.

(c) Chromium. In regard to chromium, the statements already made on pages 3-4 cannot be much elaborated. Nor yet can this method be recommended. While it is true that the metal will behave as stated, and can be easily deposited out of the solution as an amalgam, it is very hard to wash quickly enough to avoid its decomposition, and in very few cases is it possible to get it weighed without the chromium separating out. Another great objec-

tion to the method is that the weight of the mercury cathode and the container used, is so large as to make its accurate weighing a very difficult matter, and consequently a large chance for error is introduced. To avoid this, the electrolysis was carried out in a cup with a stop cock at its base for an outlet, with the idea that the amalgam could be drained off from the cup after the action was complete without the interruption of the current. By letting it drop into alcohol and ether it could thus be easily washed and dried and then weighed in a very light container. This would have done very well, as a stopcock sufficiently large for the amalgam to pass through was used, but for the fact that, although a platinum wire was used as a connection, on draining off the amalgam, small particles would adhere to the ends of the wire, and thus no matter how careful one might be in the manipulation of the apparatus, loss would occur. This, although small in the volume of Hg. made altogether too much of an error in the increase in weight of the cathode, to give accurate results. Various other ways were tried to connect the Hg with the outside circuit, such as a carbon pencil insulated from the electrolyte by a glass tube, and a platinum wire with the same insulation, to be withdrawn after the reaction was complete. But no method was found which would obviate this difficulty, and as the method was at the best, a laborious process, and not very reliable even under the best conditions obtainable, it was given up, and the chromium determined by precipitation as $Cr(OH)_3$, which, when the Nickel was present in the solution, left this metal in the best state possible for its determination.

VI. DETAILED PROCEEDURE OF DETERMINATION,
and
VARIOUS PRECAUTIONS TO BE OBSERVED.

It might be well, in a discussion of this kind, to include a complete electrolysis for the benefit of those who are carrying through such a process for the first time, as at every manipulation throughout the determination, there are points of technique, which in themselves, do not amount to much, but taken as a whole, constitute the background of the entire method. Using a copper-chromium-nickel alloy as one which typifies the entire method, a 100 cc. aliquot part of the solution as described on page 12, is taken as the starting point. A 150 cc. beaker is the best size in which to carry out an electrolysis of this volume, fitted with cover glasses which have been split in the center with a glass cutter, and notches filed in them at the right intervals to allow the protrusion of the electrodes from the beaker. Since this solution has already been acidified to the right amount in evaporating it down to SO_3 fumes, no furthur addition of acid is necessary, and the cell containing the solution together with one to two gms. of urea is subjected to electrolysis with a current of three amperes and four volts, using the electrodes as described above. In no case should the acid concentration be above 5 cc. in 100, or the copper will be deposited in spongy form. On allowing the current to run 5-10 minutes in excess of the time calculated, it is then cut down by means of the resistances provided, to a few tenths of an ampere, and the cover glasses carefully rinsed into the beaker. Here is where the only quick work needs to be done. The

current is cut off from one of the cells at a time, the electrodes raised directly above the beaker out of the solution, and washed as quickly as possible with a stream from a wash bottle, Speed is essential, as the acid solution is likely to dissolve an appreciable amount of the copper from the cathode, as soon as the current is broken. Various have shown, that if the manipulation is rapid, the loss in weight of the deposit does not amount to over three or four tenths of a milligram at the most, which is inappreciable in a half gram deposit. In fact, it has been shown by weighing the cathode before and after immersion, and washing under conditions similar to this, that this amount of weight lost is a fairly constant factor, and can be added to the deposit without fear of error. The old method of siphoning, while it may be a trifle more accurate, is not applicable here, as the residual solution must be carefully saved and in order to get it transfered by this method, such a large volume of liquid is necessary that several hours would be lost in evaporation to the right volume for the next analysis.

When the cathode has been washed free from all adhering solution, it is next rinsed in alcohol and dried at 100°C., in an oven, after which it is cooled and weighed. The remaining solution, if it contains chromium, is then neutralized with ammonia, and the chromium precipitated in the usual way. This precipitation, if there is much of the metal present, must be repeated several times in order to free the solution from the chromium and avoid the dragging down of any nickel along with it. At this point, the filtrate from the chromium precipitation corresponds to the residual solution from the copper determination, when there is no

chromium present, and hence, from here on, the methods for the two are the same. To the neutralized filtrate, is added 25-30 ccs. excess of ammonia, and five grams of $(NH_4)_2SO_4$, after which it is electrolyzed at three amperes and four volts, until the color of the liquid has entirely disappeared, and a drop on a white plate shows no color with dimethylglyoxime. The cathode is then treated in the same way as in the determination of copper, and the increase in weight taken as the amount of nickel in solution. This completes the electrolysis of the alloy, giving a rapid and accurate determination of the metals present.

VII.ACCURACY AND SPEED OF THE METHOD.

In support of this method for a commercial scheme of analysis, it will be well to note the results of the following data, which, while not being checked up against a known weight of metal in solution, has the test of accuracy firmly established by the totals of the various constituents and agreement between two checks on the same sample. The author also made an analysis of thirty five additional alloys, mostly ternary, in which he averaged on each alloy, including the sampling of the metal, three and three quarters hours work in time actually spent in the laboratory. Figuring the time as worth fifty cents an hour, it can be seen that the cost per alloy for analysis was less than two dollars, which compares very favorably with the amount and cost of the work if it were done by gravimetric or even volumetric methods.

Hence in the above, we have a speedy and accurate method of analysis on a commercial scale, one that is cheap and simple,

inasmuch as it does not require the use of expensive or experienced workers to get the acid concentration and voltages at their proper adjustment. For with the use of gauze electrodes, a deposit can be weighed with accuracy which could not have been washed under the old method without the loss of so much metal as to make the determination worthless.

VIII.CONCLUSION.

In conclusion, it would be well to state that while the above processes have been satisfactorily worked out, there still remains much to be done to make the operation more speedy at its slowest point, viz., the removal of the chromium. If one who is interested in this subject, would at some future date, determine the conditions under which nickel could be electrolyzed, in the presence of chromium, without introducing any objectionable elements, chromium could then be determined by oxidation and titration with Potassium Iodide and Sodium Thiosulfate. This would make this type of alloy capable of analysis by one of the most speedy methods in existence, Let us here express a hope that work along this line will not be discontinued, but that processes for the complete determination of other combinations of metals will be completely investigated, inasmuch as this is so superior to the methods of analysis commonly used.

DUPLICATE ANALYSES.

Binary Alloys of Copper and Nickel.

Alloy No.	Weight of Sample.	% Cu.	% Ni.	Total %.
1(a)	0.9480 gms.	99.32	0	99.32
1(b)	0.9480 "	99.23	0	99.23
2(a)	0.8610 "	90.84	8.80	99.64
2(b)	0.8610 "	90.80	8.80	99.60
3(a)	1.3990 "	81.00	18.74	99.74
3(b)	1.3990 "	81.14	18.79	99.93
4(a)	0.9048 "	71.20	28.43	99.63
4(b)	0.9048 "	71.13	28.49	99.62
5(a)	0.9174 "	61.83	38.25	99.98
5(b)	0.9174 "	61.70	38.45	100.15
*6(a)	0.9376 "	48.93	49.99	98.92
*6(b)	0.9376 "	48.99	49.83	98.82
7(a)	1.0373 "	69.59	30.55	100.14
7(b)	1.0373 "	69.53	30.63	100.16
8(a)	1.1779 "	41.17	58.23	99.40
8(b)	1.1779 "	41.11	58.31	99.42
9(a)	1.3545 "	20.65	79.35	100.00
10(a)	1.5582 "	10.53	88.90	99.43
10(b)	1.5582 "	10.60	88.90	99.50
11(a)	0.9690 "	00.00	99.72	99.72
11(b)	0.9690 "	00.00	99.60	99.60

*Contained 0.66 % SiO_2.

Each of the above contained slight traces of Fe and SiO_2.

Analyses of Ternary Alloys.

Chromium-Copper-Nickel

Alloy No.	Wt. of Sample.	% Cu.	% Cr.	% Ni.	Total %.
12.	0.5000 gms.	94.20	6.08	0.00	100.28
13.	0.8502 "	84.36	7.79	9.28	101.43
14.	1.0000 "	74.63	8.25	16.05	98.93
15.	1.2480 "	66.32	10.63	22.94	99.89
*16.	1.1720 "	54.71	15.94	29.35	100.00
17.	1.0953 "	42.56	10.13	48.00	100.69
18.	1.3166 "	32.69	13.97	54.16	100.82
19.	1.1411 "	20.85	11.80	66.25	98.90
*20.	0.5665 "	11.83	11.90	76.27	100.00
21.	1.1645 "	00.00	19.37	78.99	98.36
22.	0.7653 "	87.93	13.15	00.00	100.08
23.	0.8542 "	10.56	80.58	9.38	100.52
24.	0.5000 "	56.30	14.56	29.24	100.10
25.	0.5009 "	66.92	13.62	19.20	99.74
26.	0.5000 "	44.16	19.30	36.34	99.72
27.	0.5000 "	24.12	47.54	26.28	97.94
28.	0.50000 "	22.20	19.86	57.36	99.42
29.	0.5000 "	10.88	19.64	68.62	99.14
30.	0.8118 "	00.00	21.52	76.95	98.47
31.	0.7644 "	89.82	9.84	00.00	99.66
32.	1.1706 "	73.63	17.66	7.95	99.24
33.	0.5000 "	59.26	22.00	19.48	100.74
34.	0.5000 "	45.70	25.10	29.52	100.32
*35.	0.5000 "	33.76	29.46	36.78	100.00
36.	0.5000 "	22.58	28.10	48.42	99.10

Analyses of Ternary Alloys

Chromium-Copper-Nickel.

Alloy No.	Wt. of Sample.		% Cu.	% Cr.	% Ni.	Total %.
37.	0.5000	gms.	16.90	29.70	58.12	99.72
38.	0.5000	"	0.000	28.44	71.56	100.00
40.	1.0424	"	70.57	19.93	8.99	99.49
#41.	0.8622	"	54.16	31.63	14.21	100.00
42.	0.5000	"	33.60	38.16	26.78	98.54
43.	0.5000	"	22.68	41.32	34.60	98.60
44.	0.5000	"	11.02	43.30	46.46	100.78
45.	0.4510	"	00.00	44.93	56.55	101.48
48.	0.5000	"	28.42	54.92	17.12	100.46
51.	0.5000	"	00.00	57.40	41.66	99.06

*Nickel determined by difference.

#Chromium determined by difference.

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